INVESTIGATION OF DISSOLUTION AND DEPOSITION OF COPPER IN THE SOLID ELECTROLYTE $RbCu_4Cl_3I_2$

Gennady I. OSTAPENKO
Institute of Radio Engineering and Electronics, Ulyanovsk Division, Russian Academy of Sciences; 48, Goncharov Str., Ulyanovsk 432011, Russia
E-mail: ufire@mv.ru

Now rather extensive experimental data about kinetics of electrochemical processes on the copper electrode in Cu^+-conducting solid electrolytes are accumulated (1-3). However, the interpretation of these results is inconsistent.

The purpose of represented work is the potentiostatic investigation into kinetics of electrochemical dissolution and deposition on the $Cu/RbCu_4Cl_3I_2$ interface.

Potentiostatic transients of copper anodic dissolution at low potentials are typical for formation and growth of nuclei. The initial sites of such transients are described by $i \propto t^n$ dependence, where n determines law of formation and growth of nuclei (4). Is found out that n increase approximately from 1 up to 2 with increasing potential. At anodic dissolution the two-dimensional growth of nuclei is possible only. Hence, at rather low potentials and short times, the current varies according to the law (4):

$$i = \pi q N_0 V_1^2 t,$$

where q is the dissolving layer charge, N_0 is the quantity of the instantaneously formed nuclei and V_1 is the advance rate of the dissolution front along the electrode surface. Apparently, at higher potentials alongside with the instantaneously formed nuclei arises new nuclei with rate A and consequently the law of the current change with the time aspires to square-law (4):

$$i = \pi q V_1^2 A t^2. \qquad [1]$$

The dependence of the current on the time becomes less expressed with the potential increasing, and at potentials more than 120 mV this dependence generally disappears. Hence, at potentials more than 120 mV, the copper anodic dissolution is limited by slowed charge transfer. Accordingly, current-voltage characteristics (CVC) at these potentials is described by the known equation:

$$\ln \frac{i}{1 - \exp \frac{e}{kT}\eta} = \ln i_0 + \alpha \frac{e}{kT}\eta \qquad [2]$$

with the exchange current density $i_0 = 2.7$ mA cm^{-2} and anodic transfer coefficient $\alpha_a \approx 0.45$.

From potentiostatic transients of the copper cathodic deposition it follows that the value of n, which determines the law of the current change with the time, makes 1.9±0.1. Hence, the copper deposition can be determined by progressing formation and two-dimensional growth of nuclei according to Eq. [1] or instantaneous formation and three-dimensional growth of nuclei (4):

$$i = \frac{e\rho}{m_0} V_1^2 V_2 \pi N_0 t^2, \qquad [3]$$

where V_2 is the growth rate of needles and dendrites.

It is known, that the reversible and inert electrodes in solid electrolytes behave identically at cathodic deposition (5) and the growth of needles and dendrites is observed at deposition (6). These facts guess, that the deposition of copper on copper happens according to Eq. [3] at instantaneous formation and three-dimensional growth of nuclei, i.e. needles and dendrites.

At formation and three-dimensional growth of nuclei and at the time tending to zero (4):

$$i_{t \to 0} = \frac{e\rho}{m_0} V_3,$$

where ρ is the density, m_0 is the atom mass of copper and V_3 is the growth rate of thickness of the electrode starting sheet. At rather lengthy times (4):

$$i_{t \to \infty} = \frac{e\rho}{m_0} V_2.$$

From the potentiostatic transients of copper cathodic deposition it follows that the currents $i_{t \to 0} \approx 0$ at low potentials. Hence, the electrode thickness is not incremented, but the needles and dendrites intensively grow on its surface. These currents occur and are incremented with the potential at potential increasing. V_2 and V_3 for various potentials are calculated. From these calculations it follows that the growth rate of needles and dendrites exceeds greately the growth rate of the deposit thickness at rather low potentials. The difference of rates is reduced with increasing of the potential, they are also compared at potentials more than 80…100 mV. Hence, at these potentials and the higher ones, the needles and dendrites practically do not grow, and the thickness of the starting sheet is increased.

The quantity of nuclei increases with potential increasing (4). At some value of potential there will occur a state, at which the further increasing of quantity of nuclei will become impossible, since each atom on the electrode surface will be a nucleus. Therefore dissolution and deposition of copper should be limited by slow charge transfer at potentials above indicated. Really, the CVC of copper deposition at potentials higher than 120 mV is described by Eq. [2] at $i_0 = 2.7$ mA cm^{-2} and cathodic transfer coefficient $\alpha_c \approx 0.55$.

Cathodic and anodic CVCs significantly differ at potentials below 100 mV, i.e. their considerable asymmetry is observed. It is caused, apparently, by various mechanisms of crystallization, since at anodic dissolution takes place two-dimensional growth of nuclei, and at cathodic deposition - mainly three-dimensional growth of needles and dendrites.

REFERENCES

1. R.D. Armstrong, T. Dickinson and K. Taylor, *J. Electroanal. Chem.*, **57**, 157 (1974).
2. N.N. Vershinin, Yu. I. Malov and E.A. Ukshe, *Elektrokhimiya USSR*, **18**, 255 (1982).
3. F.I. Kukoz, A.M. Kolomoets and V.P. Kuz'min, *Elektrokhimiya USSR*, **16,** 1861 (1980).
4. J.A. Harrison and H. Thirsk, in *Electroanal. Chem.*, A.J. Bard Ed. vol. 5, p. 67, Decker, New York (1971).
5. B. Scrosati, in *Solid State Batteries*, Proc. NATO Adv. Study Inst., Alcabideche, Sept. 2-14, 1984, p. 109, Dordrecht e.a. (1985).
6. J.M. Schemilt, B.C.H. Steele and J.E. Weston, *Solid State Ionics*, **2**, 1 (1981).